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**REINFORCING POLYOLEFIN FIBER, USE AND PRODUCTS
COMPRISING THE FIBER.**

The present invention relates to the field of hydraulic-setting materials and
10 more particularly to products based on a hydraulic binder and fibers.

These products may especially be in the form of shaped articles in the form
of boards (or plates), such as plane or corrugated boards for covering or building
elements, such as roof or wall boards, but also in other forms, especially hollow or
tubular forms.

15 Such articles may be manufactured by a technique involving the filtration of
an aqueous suspension, comprising a hydraulic-setting binder, reinforcing fibers
and, optionally, fillers. A process commonly used that relies on this technique is
known as the Hatschek process: a very dilute aqueous suspension is contained in
a tank fitted with means for uniformly distributing the constituents within the
20 volume of the tank; a filter drum is partially immersed in the tank and its rotation
causes the deposition, on its surface, of a thin film of material (fibers and hydrated
binder); this film is carried by a felt towards a size (or format) roll onto which it is
continuously wound up; when the film has reached the desired thickness, it is cut
so as to unwind from the roll an individual sheet of hydraulic-setting material. The
25 sheet may then be made in the form of a shaped product and it acquires its final
characteristics by the curing of the binder. A product of larger thickness may be
obtained by superposing a suitable number of sheets and by pressing them
together in order to ensure cohesion of the whole assembly.

For a long time asbestos has been used as fibers for forming the framework
30 of the filtered film, asbestos fibers having the property of being dispersed in the
aqueous suspension without forming agglomerates deleterious to the regularity of
the process, the said fibers being even capable of "opening up" in the aqueous
medium so as in this way to constitute, at the surface of the drum, a highly
entangled filtering network capable of retaining the hydraulic binder particles,

including the fines, with a very high filtration efficiency. Asbestos fibers also have good tensile strength properties, which contribute to the mechanical properties of the final product when mainly stressed in bending. Asbestos fibers therefore have two functions, namely a framework function (in the sense of forming a filtering network) and a reinforcement function (which contribute to the final mechanical properties). Asbestos is furthermore a highly competitive material from the cost standpoint.

However, this material is tending to be discarded from the manufacture of a large variety of common consumer products and from the building field for public health reasons.

For this reason, there is a demand for a replacement material that does not have the drawbacks of asbestos.

However, at the present time, it has not been possible to find a natural or synthetic fibrous material capable of fulfilling the same role as asbestos, that is to say one that combines filtration capability, mechanical properties and resistance to the alkaline medium of hydraulic-setting substances.

Cellulose fibers prove to be suitable for forming a framework of filtration of the mineral binder particles, but are inadequate from the mechanical reinforcement standpoint.

Glass fibers have an intrinsic mechanical strength, but are generally sensitive to attack by the alkaline medium of the hydrated mineral matrix, which means modifying the matrix by additives intended to protect the glass and/or using an alkaline-resistant glass suitable for such aggressive environments. However, these solutions involve a not insignificant cost burden.

PVA (polyvinyl alcohol) or PAN (polyacrylonitrile) fibers are also envisaged as reinforcing fibers, to complement possible filtration fibers, but they also have an economic disadvantage associated with the cost of the raw material.

Polypropylene fibers would be good candidates as reinforcing fibers, as they are less expensive and do have a high mechanical strength. However, they exhibit a rather mediocre reinforcement effect in a matrix of a hydraulic-setting mineral binder, because of a low affinity of the lipophilic olefin material for hydrophilic hydrated matrices.

Many attempts have been made to improve this interaction.

Thus, it has been attempted to modify polypropylene by means of organic or mineral additives introduced into the mass of the polymer.

This modification inevitably results in an increased cost of the fibrous raw material and a not insignificant effect on the intrinsic properties of the fibers
5 especially a lowering of the mechanical properties.

Another modification approach consists of surface treatments, such as texturizing, sandblasting, corona effect, etc. These solutions considerably complicate the fiber manufacturing process and are generally of no interest from the economic standpoint.

10 The present invention aims to provide a reinforcing fiber for hydraulic-setting products, which has good reinforcing properties while still remaining inexpensive.

The invention relies on the fact that a simple modification of the exposed surface of the fibers by a suitable size effectively and lastingly improves the interaction between the fibers and the matrix. Since the amount of material
15 provided by the size is minimal compared with the weight of fibers, this modification does not substantially increase the cost of the fibrous material.

In this regard, the subject of the invention is a fiber as claimed in claim 1.

According to the invention, the surface properties of the filaments constituting the polyolefin fiber are modified by one or more sizing agents bringing three
20 functions, that of assisting the fiberizing operation, that of being able to be wetted by the hydraulic-binder-based composition, and that of promoting adhesion to the hydraulic-setting matrix.

In the present application, the term "fiberizing" means in general the manufacture of the polyolefin fiber, starting at the die or spinning of the molten
25 material, passing through a drawing stage and going until at least the chopping of chopped yarns.

The function of assisting in the fiberizing operation consists in making it easier to form the polyolefin fiber from polyolefin filaments, at least at one stage of the fiberizing operation: this especially involves the lubrication of the filaments in
30 order to improve their handling by the yarn transporting and assembling members at various stages in the manufacture of the fibers, the minimizing of the electrostatic charges carried by the filaments, so as to allow them to be assembled into a yarn, or the providing of the cohesion or integrity of the yarn formed by the assembly of filaments.

The function of being able to be wetted by the hydraulic-binder-based composition consists in facilitating the dispersion of the polyolefin fibers in the matrix, ensuing from the good dispersion of the fibrous material within the initial binder/water mixture from which the product is manufactured. This function 5 principally relies on the surface polarity of the fibrous material in order to make it hydrophilic.

The function of promoting adhesion to the hydraulic-setting matrix consists in increasing the interaction between the fibrous reinforcement and the matrix of the hardened product. The latter function also relies on the presence of polar 10 functional groups on the surface of the fibers.

These functions may be provided by one or more agents chosen from lubricants, antistatic agents, surfactants, fatty-chain compounds and polymers having polar functional groups, in which a lubricant may be a fatty-chain compound, likewise a surfactant may be a fatty-chain compound, or an antistatic 15 agent may be a polymer having polar functional groups.

Thus, it has been found, quite surprisingly, that agents or mixtures, especially lubricants or antistatic agents or surfactants, which could be intended for use as fiberizing or spinning agents for textile materials that are not necessarily synthetic, give olefin fibers considerable reinforcing properties for reinforcing hydraulic-20 binder-based products.

The size may comprise polyalkylene glycols having lubricating properties, particularly polyethylene glycol or polypropylene glycol.

As surfactants, nonionic or ionic, anionic or cationic, surfactants may be considered.

25 The size advantageously comprises amine or polyamine compounds, phosphoric or polyphosphoric compounds, phosphate or polyphosphate compounds having antistatic properties, in which the amine or phosphoric functional group may have an adhesion promoter effect by complexation of calcium ions from the hydraulic-setting substance, tending to create a strong 30 interaction between fiber and matrix.

Fatty-chain compounds are compounds comprising an optionally substituted hydrocarbon chain of at least 9 carbon atoms, especially 10 to 24 carbon atoms, which may in particular be derived from natural oils, such as coconut oil, palm oil, etc. They may be based on fatty alcohols, ethers of fatty alcohols, fatty acids,

esters of fatty acids and amides of fatty acids, in which the fatty chain preferably is a C₁₀-C₂₄ chain. They are, where appropriate, (poly)alkoxylated, especially (poly)ethoxylated or (poly)propoxylated, or glycerol derivatives.

These compounds have the advantage of having a hydrocarbon part with
5 good affinity for the polyolefin material of the fiber, whereas another part of the compound may be functionalized in order to provide a required function.

Thus, the size may include a polyfunctional agent, which is a product of combination of functional radicals (especially the aforementioned lubricants or antistatic agents) with fatty-chain residues, derived especially from a natural oil, in
10 order to provide together several of the intended functions of the invention. These residues may be based on fatty alcohols, ethers of fatty alcohols, fatty acids, esters of fatty acids, in which the fatty chain is preferably a C₁₀-C₂₄ chain.

Thus, polyalkylene glycols derived from fatty acids, in which the fatty chain advantageously comes from or is derived from a natural oil, are envisaged. Fatty
15 amines, esters of phosphoric acid based on a fatty chain, and esters of fatty acids having a quaternary ammonium functional group (esterquats derived from fatty acids and from triethanolamine), in which the fatty chain advantageously comes from or is derived from a natural oil, are also envisaged.

Polyethoxylated amides, whether or not based on fatty acids, are also
20 envisaged.

The size agent or agents may also be chosen from polymers having polar functional groups, especially water-dispersible or in emulsion, of the olefin type modified by polar groups by copolymerization or by post-synthesis grafting. For example, mention may be made of a halogenated polymer (particularly a
25 polyolefin), such as chlorinated polypropylene, or a polyolefin grafted by a polar group, especially of the epoxide type, such as polypropylene grafted with glycidyl methacrylate.

The polyolefin fibers are preferably polyethylene or polypropylene fibers, more particularly polypropylene fibers.

30 The polyolefin does not need to be modified by organic or mineral additives in order to make it compatible with the hydraulic-setting matrix, this function being provided by the size. However, for particular applications, it may be envisaged to incorporate additives or modifying fillers, especially hydrophilic additives, into the

matrix. Furthermore, all the additives or fillers commonly used for fiberizing the polyolefin, in particular those intended to facilitate fiberizing, may be included.

A more particularly advantageous reinforcing effect has been observed with polyolefin fibers of relatively small cross section, expressed by a titer of about 0.5
5 to 10 dtex, more advantageously 0.5 to 2 dtex.

The cross section of the fibers is not necessarily circular and may have an irregular or multilobate shape.

In one particularly advantageous embodiment, the polyolefin fiber has a high tenacity, of at least 4 cN/dtex, preferably at least 5 cN/dtex, very preferably at least
10 7 cN/dtex, and particularly from 8 to 9 cN/dtex. This tenacity range may be achieved by adjusting the polyolefin fiberizing or spinning and drawing process in an appropriate manner. A base polyolefin material may be specifically chosen to have a suitable molecular weight distribution.

The fibers are generally in the form of chopped yarn with a length of around 2
15 to 20 mm, in particular 5 to 10 mm.

The total amount of sizing agent(s) present on the fiber is generally around 0.05 to 5% by weight, especially around 0.1 to 2% by weight, of dry matter relative to the weight of polyolefin.

The sizing agent or agents may be applied to the polyolefin fiber in one or
20 more stages over the course of the fiberizing process, as the fiber leaves the die or spinneret, during its transportation, during the drawing step, during the chopping operation and/or when the fiber is being unwound from a bobbin of polyolefin yarn.

The or each size may be applied in the form of a pure liquid or as a solution, dispersion or emulsion, aqueous-based or based on another suitable vehicle,
25 especially aqueous-based with an organic, preferably polar, co-solvent, by spraying or passing through a bath.

In the case of the use of an aqueous composition or one based on another vehicle, the concentration of the composition is advantageously around 0.5 to 50% of the solids relative to the total weight of the composition. The concentration will
30 advantageously be low when the size is applied by spraying.

The subject of the present invention is also the use of a fiber as described above, as reinforcing fiber in a product based on fibers and a hydraulic-setting substance, and also a product thus formed.

The hydraulic-setting substance is formed from a hydraulic-setting binder, mainly chosen from various existing cements, to which inert or active fillers may optionally be added.

Among fillers and additives, mention may be made of rheology-modifying 5 additives (dispersants, plasticizers, superplasticizers, flocculants), mineral fillers (silica, fly ash, slag, pozzolans, carbonates), as well as support or framework fibers for filtration or draining (or dewatering) processes (natural fibers, especially cellulose fibers, or synthetic fibers).

The fibers according to the invention are effective as reinforcement in 10 proportions that do not have to be increased compared with more expensive fibers, that is to say around 0.2 to 5% by weight of reinforcing fibers relative to the total dry weight of the initial mixture.

This product may be in various forms, preferably in the form of a plane (or flat) or corrugated board (or plate).

15 The subject of the invention is also a process for manufacturing such a product. According to this process, an initial mixture based on hydraulic binder, water and fibers is prepared, the mixture is filtered over a fixed or moving support, in order to form a wet elementary sheet, a plurality of elementary sheets are optionally superposed to form a wet intermediate product and the sheet or the wet 20 intermediate product is dried.

Finally, the subject of the invention is a composition for a hydraulic-setting material comprising a hydraulic binder and fibers as described above. These compositions may be cementitious preparations to be put into suspension for the dewatering process, or cementitious preparations for mortars comprising particles, 25 including sand for other forming processes.

The invention will now be described in a nonlimiting manner in the following examples.

EXAMPLE 1

A polypropylene fiber with a titer of 0.75 dtex was manufactured, a size 30 containing a mixture of products of the SILASTOL reference sold by Schill & Seilacher and which were emulsions being applied to the filaments.

The size contained :

- 80% by weight of the product having the reference Cut5A, based on an ester of a fatty-acid-derived polyglycol ;

- 20 % of the product having the reference Cut5B, based on a fatty alcohol phosphate.

The size was applied to the polypropylene filaments during fiberizing, as they left the die or spinneret, in an amount of 0.3% by weight of solids relative to the dry weight of polypropylene.

The yarn formed by the assembled polypropylene filaments was transported by means known from textile fiber manufacturing processes, and then drawn, before being chopped into 6.6 mm lengths.

This fiber had a tenacity of greater than 9 cN/dtex.

10 The adhesion of this fiber to a cementitious matrix was assessed by a laboratory test in which a fiber is coated with a mortar, leaving the ends of the fiber free, the mortar undergoes a curing operation and then the ends of the fiber are pulled, the tensile force and the displacement of the point(s) of pulling being measured. The maximum force before fiber pull-out is used to determine the 15 strength of adhesion, while the slope of the curve in which the force is plotted as a function of the displacement at the point corresponding to fiber pull-out is used to determine the slip stress, which is characteristic of the adhesion between the fibers and the matrix.

The details of the preparation were the following :

20 A mortar containing 500 g of CPA 52.5 cement, 500 g of fine sand ($D_{50}=254 \mu\text{m}$ according to ASTM E.11/70), 98 g of calcium carbonate and 250 g of water was prepared.

A stretched fiber was placed in a parallelepipedal mold, with the fiber well-centered, and the mortar was cast around the fiber, without breaking the fiber. The 25 mold was placed in a sealed bag.

The cure was carried out for 48 h at 20 °C and 95% relative humidity in a maturing chamber in which the mortar sets. The contents were then demolded from the molds and placed with a little water in a heat-sealed bag kept at 40°C. The measurements were carried out on the 7th day, that is to say after 5 days at 30 40°C.

The results are given in Table 1 below.

COMPARATIVE EXAMPLE 1

For comparison, the same on-fiber tensile test was carried out with a polypropylene fiber of 2.7 dtex sold as a concrete anticracking agent, sold under

the brand name CRACKSTOP by Sika. These fibers provide no structural reinforcement of the concrete – they limit cracking upon shrinkage and increase the impact strength and impermeability of the cured material.

The results are given in Table 1 below.

5 EXAMPLE 2

The same tensile test was carried out on a 1 dtex polypropylene fiber 8 mm in length, of moderate tenacity (about 5 cN/dtex), obtained by a one-step spinning-drawing process and containing a spinning size with the reference SYNTHESIN 7292 sold by the company Dr. Boehme, in an amount of 0.4 % by weight of dry 10 matter relative to the weight of polyolefin.

The size comprised fatty-acid polyethylene glycol ester and phosphoric acid ester compounds, natural-oil-based.

The results are given in Table 1 below.

Table 1

15

| Example | Adhesive strength (MPa) | Slip stress (MPa) |
|---------|----------------------------|----------------------|
| 1 | 0.26 | 0.16 |
| 2 | 0.44 | > 0.60 |
| Comp. 1 | 0.20 | 0.19 |

These results show that the fibers of examples 1 and 2 have better adhesion to the matrix, and also an improved slip stress in the case of the fiber of example 2.

20 Comparisons with other commercial fibers for concrete, such as DIMAPOS fibers from Istrochem, SIRIOFIBRE fibers from Proind, ISOCRETE and FIBERLOCK fibers from Etruria, DAIWABO POLYPRO fibers from Daiwabo and MERAKLON fibers, show results of the same order as those of comparative example 1.

25 EXAMPLES 3 to 14

These examples illustrate the application of various polypropylene fibers according to the invention to the manufacture of a cementitious product by filtration. The products were manufactured by a laboratory method reproducing quite faithfully the main characteristics of the products obtained by industrial 30 methods, such as the Hatschek technique.

A cementitious composition based on the following cement matrix was prepared:

| Components | Mass (in g) |
|--------------------------------|-------------|
| CPA cement (95% clinker) | 79.2 |
| Calcium carbonate | 15.5 |
| <i>Pinus Radiada</i> cellulose | 3.5 |
| Polypropylene fibers | 1.8 |
| BASF AE70 flocculant | 400 ppm |
| Total | 100 |

put into suspension with a large excess of water.

5 The composition was filtered through a metal mesh in order to form an individual layer approximately 1 mm in thickness. Six individual layers were superposed and subjected to a pressing cycle in order to obtain a material containing, before setting, about 50% by weight of water relative to the weight of the cement, and having a thickness of about 6 mm.

10 This laboratory material was cured for 6 days at 40°C in a sealed bag, before being cut into test pieces 20 mm in width and more than 200 mm in length, which test pieces were placed in cold water for 24 hours before being mechanically stressed in tension.

The tested fibers had the following characteristics:

15 EXAMPLE 3

This example used the same moderate-tenacity fiber as in example 2.

EXAMPLE 4

This example used the same high-tenacity fiber as in example 1, except for a higher titre (or linear mass), which was 1 dtex.

20 EXAMPLE 5

This example used a high-tenacity fiber similar to that of example 4, except that it was obtained by applying a post-size, downstream of the drawing stage and before the chopping stage. This post-size was based on a lubricating and antistatic mixture sold under the reference KB 144/2 by Cognis. It was applied in an amount of 0.9% of dry matter relative to the weight of polypropylene.

EXAMPLE 6

This example used a high-tenacity fiber similar to that of example 5, except that the post-size was based on a chlorinated polypropylene sold by Eastman. It was applied in an amount of 0.6% by weight of dry matter relative to the weight of polypropylene.

5 **EXAMPLE 7**

This example used a high-tenacity fiber similar to that of example 5, except that the post-size was based on a polypropylene grafted with glycidyl methacrylate. It was applied in an amount of 1% by weight of dry matter relative to the weight of polypropylene.

10 **EXAMPLE 8**

This example used a high-tenacity fiber similar to that of example 7, with another polypropylene grafted with glycidyl methacrylate.

EXAMPLE 9

This example used a high-tenacity fiber similar to that of example 4, except
15 that it was obtained with a spinning size based on a fatty-acid-derived polyethylene glycol ester sold under the reference STANTEX S6077 by Cognis, applied in an amount of 0.5% by weight of dry matter relative to the weight of polypropylene. It also included a post-size was based on a chlorinated polypropylene, which was applied in an amount of 1.2% by weight of dry matter
20 relative to the weight of polypropylene.

EXAMPLE 10

This example used a high-tenacity fiber similar to that of example 9, except that the post-size was based on the polypropylene grafted with the glycidyl methacrylate of example 7. It was applied in an amount of 1% by weight of dry
25 matter relative to the weight of polypropylene.

EXAMPLE 11

This example used a high-tenacity fiber similar to that of example 10, with a post-size based on the polypropylene grafted with the glycidyl methacrylate of example 8.

30 **EXAMPLE 12**

This example used a high-tenacity fiber similar to that of example 4, except that it was obtained with a spinning size based on non-ionic surfactants and esterquats, this being sold under the reference STANTEX S6087/4 by Cognis, applied in amount of 0.5% by weight of dry matter relative to the weight of

polypropylene. It also included a post-size identical to the spinning size, which was applied in an amount of 1% by weight of dry matter relative to the weight of polypropylene.

EXAMPLE 13

5 This example used a high-tenacity fiber similar to that of example 12, except that it was obtained by applying a spinning size and a post-size based on the same commercial product sold under the reference SYNTHESIN 7292 by the company Dr Boehme, used previously in example 2 .

10 EXAMPLE 14

This example used a high-tenacity fiber similar to that of example 12, except that it was obtained by applying a spinning size and a post-size based on the same product under the reference KB 144/2 by Cognis used previously in example 5.

15 COMPARATIVE EXAMPLE 2

For the purpose of comparison, the same mechanical tests were carried out with laboratory products in which the polypropylene fibers were replaced with a 2.2 dtex PVA fiber having a length of 6 mm and a tenacity of 12 cN/dtex, sold by Sichuan.

20 COMPARATIVE EXAMPLE 3

For the purpose of comparison, the PP fiber used in comparative example 1 was used for mechanical tests in the laboratory products.

25 The tensile tests were carried out by fitting the test pieces between the jaws of a tensile testing machine with a distance of 200 mm between jaws. The tensile test was carried out at a pull rate of 1.2 mm/min.

The force/displacement curve was plotted, this having a shape typical of the results observed with products obtained by the Hatschek technique.

30 At the start of the displacement, the force rapidly increases and then a plateau is observed in which the force changes slowly, corresponding to the multicracking of the test piece, until a macrocrack appears, after which the force drops by the slip effect during opening of the macrocrack.

The length of the multicracking plateau reflects the effect of the board reinforcement by all the fibers. The slope of the force-displacement curve in the latter part of the test was used to determine the slip stress, which is characteristic

of the adhesion between each fiber and the cementitious matrix. The slip stress was calculated by applying a correction factor of 0.64 for the orientation of the fibers.

The results of the tests are given in Table 2 below.

5

Table 2

| Example | Length of the multicracking plateau (in mm) | Slip stress (in MPa) |
|---------|---|----------------------|
| 3 | > 10 | > 1.3 |
| 4 | 3 | 0.35 |
| 5 | 6 | 0.6 |
| 6 | 11 | > 1.5 |
| 7 | 9 | > 1 |
| 8 | 9 | > 1.5 |
| 9 | 11 | > 1.5 |
| 10 | 10 | > 1.3 |
| 11 | 11 | > 1.2 |
| 12 | 12 | > 1.3 |
| 13 | 12 | > 1.1 |
| 14 | 10 | > 1.3 |
| comp. 2 | 7 | > 1.5 |
| comp. 3 | < 0.2 | < 0.2 |

This shows that much better results are obtained with examples 4 and 5
10 than with the Crackstop fiber of comparative example 3.

The performance of example 3 and 6 to 14 as regards adhesion to the matrix is of the same order or even better than for PVA, with a base material (polypropylene) costing much less.

EXAMPLES 15 and 16

15 These examples illustrate the application of polypropylene fibers according to the invention in the manufacture of a cementitious product by the Hatschek process.

Example 15 used the same high-tenacity fiber as example 4.

Example 16 used the same fiber as in example 3.

An aqueous suspension based on the same matrix as in examples 3 to 14 was prepared. This suspension was introduced into the tank of a Hatschek machine, for the formation of a film and for the winding onto a size (or format) roll 5 of a sheet of hydrated cementitious material approximately 1 mm in thickness. After cutting, sheets of hydrated material were superposed on a form so as to form plane or corrugated boards having a thickness of 6 mm.

The boards were subjected to mechanical tests after a 28-day cure at room temperature.

10 Test pieces having the same dimensions as those of examples 3 to 14 are subjected to tensile tests under the same conditions. The force-displacement curves were of similar shape, with a multicracking plateau and a decrease after pull-out.

15 The absolute values of the measured slip stresses were slightly lower than in tests 3 and 4, for reasons due to the orientation of fibers and to the method in which the stresses were calculated. However, in example 16, an improvement was observed compared with example 15, with a slip stress increased by a factor of more than 3, as had been observed in the laboratory tests of examples 3 and 4.